1922
D29

THE CATALYTIC PREPARATION OF DIPHENYL ETHER

MIXED DIALKYL MERCURY COMPOUNDS

BY

JOHN BLACKWELL DAVIS
B. S. Beloit College, 1920

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

MASTER OF SCIENCE

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

1922

Digitized by the Internet Archive
in 2016

https://archive.org/details/catalyticprepara00davi

1922
H29

UNIVERSITY OF ILLINOIS

THE GRADUATE SCHOOL

January 16 1922

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY John B. Davis

ENTITLED The Catalytic Preparation of Diphenyl Ether (and) Mixed Dialkyl Mercury Compounds

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science

Carl S. Marvel
In Charge of Thesis

W. A. Noyes
Head of Department

Recommendation concurred in*

Committee on Final Examination*

*Required for doctor's degree but not for master's

499017

ACKNOWLEDGMENT.

The writer wishes to express his sincere thanks and appreciation for Dr. Marvel's many helpful suggestions and criticisms received in the course of this work.

TABLE OF CONTENTS.

The Catalytic Preparation of Diphenyl Ether.

Introductory page 1

Historical 2

Theoretical 4

Experimental

1) Elecrtic Furnace 6

2) Catalyst 9

3) Effect of Aluminum Oxide on Phenol at High Temperatures 9

4) Effect of Aluminum Sulfate on Phenol at High Temperatures 11

Summary 12

Mixed Dialkyl Mercury Compounds.

Introduction 13

Historical 14

Theoretical 15

Experimental

1) The Preparation of Benzyl Mercury Chloride 17

2) The Preparation of Methyl Mercury Iodide 18

3) Reaction of Methyl Magnesium Iodide on Benzyl Mercury Chloride 19

4) Reaction of Ethyl Magnesium Bromide on Methyl Mercury Iodide 20

Summary 21

Part I.

The Catalytic Preparation of Diphenyl Ether.

INTRODUCTORY.

In a recent paper by A. Maihle and F. de Gordon [1] on the study of the catalytic preparation of ethers, it was shown that all the ethers of the primary aliphatic alcohols- up to the fifth member of the series- could be prepared by catalytic methods. These workers, using a Jena combustion tube and combustion furnace, obtained pure products at fairly low temperatures (200-230 degrees).

Similar methods were tried by Maihle in the preparation of some aromatic ethers, using thorium oxide as a catalyst[2]. Likewise mixed ethers have been prepared catalytically[3]. Attempts have been made to use other catalysts such as titanium oxide and zirconium oxide in the preparation of ethers and of thiophenols, none of which was as satisfactory as thorium oxide.

This work was undertaken in an attempt to develop a cheap method for the preparation of diphenyl ether. Aluminum oxide was chosen as a catalyst since it is known that aluminum phenolate, upon heating, will decompose to yield diphenyl ether.[4,5] Also, aluminum oxide is very cheap, while thorium oxide is comparatively expensive. An electric furnace was used, since this permitted better temperature control.

1. Bull. Soc. chim. 25,565(1901) 27,121(1902)
2. Comp. rend. 151,492(1910) 155,261(1912)
3. Comp. rend. 155, 261(1912)
4. Ber. 15, 359(1882)
5. J. Chem. Soc. 41,8 (1882)

HISTORICAL.

Diphenyl ether has been prepared by the use of a number of chemical reactions. Hoffmeister in 1871 first prepared this compound by the condensation of benzene diazonium sulfate with phenol.[1] It has been prepared by distilling a mixture of equal molecular amounts of sodium phenolate and sodium metaphosphate;[2] by the condensation of potassium phenolate and brombenzene;[3,4] by the use of flourbenzene and potassium phenolate;[5] by the decomposition of the ammonium salt of phenyl salicylic acid;[6] by the distillation of aluminum phenolate.[7]

A method which involves the dehydration of phenol is the action of three parts of zinc chloride on one part of phenol, which is heated in a bomb for eight hours at a temperature of 350 degrees.[8] The yield in this case was only 5-6% of the weight of the phenol. None of the above methods gave good yields and in almost every case numerous by-products were obtained.

Catalytic methods for the preparation of diphenyl ether, as well as numerous other aliphatic and aromatic ethers, have been studied quite extensively by A. Maihle.

1. Ann. 159,191 (1871)
2. Ber. 15, 1124 (1882)
3. Ber. 38, 2211 (1905)
4. Ann. 350, 85 (1906)
5. Ann. 243, 220 (1888)
6. Ann. 257, 78 (1890)
7. J. Chem.Soc. 41, 8 (1882)
8. Ber. 14, 189 (1881)

A catalytic method was described in which thorium oxide was used as a catalyst;[1] titanium oxide and zirconium oxide were both tried as catalysts by these workers, but the best results were obtained by the use of thorium oxide. Aluminum oxide has been used in the preparation of aliphatic ethers [2] but no record was found of its having been used in the preparation of diphenyl ether nor of any of the other aromatic ethers.

1. Comp. rend. 151,493 (1910)
2. Comp. rend. 6, 329 (1920)

THEORETICAL.

Since aluminum oxide has been successfully used for the preparation of aliphatic ethers,[1] it was thought that it might prove a good catalyst in the preparation of the aromatic ethers. This was chosen, also, for the reason that Gladstone and Tribe obtained a fair percentage of diphenyl ether by the decomposition of aluminum phenolate.[2] They heated 469 grs. of the material and obtained 268 grs. of distillate- of this amount, over 60% was found to be diphenyl ether. Likewise, Maihle and F.de Gordon obtained, by the use of aluminum oxide as a catalyst, diethyl ether in as high as 71% yields.[3] Dipropyl ether was prepared by the same workers with yields up to 54%. The preparation of certain mixed aliphatic ethers is also described in the literature,[4] which compounds the author claims have been prepared heretofor only by "purely chemical" methods.

The theory of the mechanism of the dehydration action is described as being analagous to the action of sulfuric acid on primary alcohols.[5]

$$C_nH_{2n+1}\cdot OH + SO_4H_2 \longrightarrow H_2O + SO_4H\cdot C_nH_{2n+1}$$

$$SO_4H\cdot C_nH_{2n+1} + C_nH_{2n+1} \longrightarrow (C_nH_{2n+1})_2O + SO_4H_2$$

$$SO_4H\cdot C_nH_{2n+1} \longrightarrow C_nH_{2n} + SO_4H_2$$

Thus the sulfuric acid is regenerated at the temperature necessary for the formation of the ether.

1. Comp. rend. 170, 329 (1920)
2. J. Chem. Soc. 41, 8 (1882)
3. Bull. soc. chim. 25, 565 (1901); 27, 121 (1902)
4. Bull. soc. chim. 27, 328 (1902)
5. Comp. rend. 150, 823 (1910)

Similar reactions are supposed to take place when such a catalyst as thorium oxide is used. The thorate and water is first formed by the action of the phenol on the oxide and the thorate in turn decomposed into the ether and the original oxide.[1]

$$2(C_nH_{2n+1}\cdot OH) + ThO_2 \rightarrow ThO(OC_nH_{2n+1})_2 + H_2O$$

$$ThO(OC_nH_{2n+1})_2 + 2R\cdot OH \rightarrow 2(R\cdot O\cdot C_nH_{2n+1}) + ThO(OH)_2$$

$$ThO(OH)_2 \longrightarrow ThO_2 + H_2O$$

Titanium oxide and zirconium oxide behave similarly. The theory of the mechanism in the preparation of diphenyl ether by the use of thorium oxide as a catalyst was similarly described.[2]

$$2(C_6H_5OH) + ThO_2 \rightarrow H_2O + ThO(OC_6H_5)_2$$

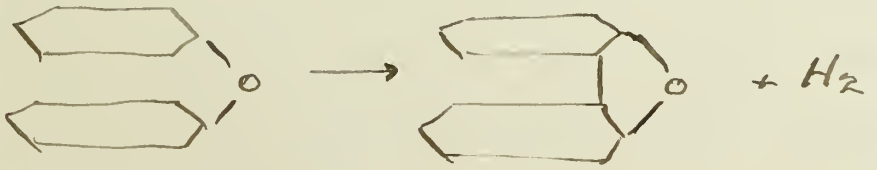
$$ThO(OC_6H_5)_2 \longrightarrow ThO_2 + (C_6H_5)_2O$$

In working with aluminum oxide it was expected that a similar reaction might take place.

$$6(C_6H_5OH) + Al_2O_3 \rightarrow 3H_2O + 2Al(OC_6H_5)_3$$

$$2Al(OC_6H_5)_3 \longrightarrow Al_2O_3 + 3(C_6H_5)_2O$$

This method, however, was not found useful because at the temperature required for the formation of diphenyl ether, a secondary reaction occurs and the diphenyl ether is converted into diphenylene oxide and hydrogen.



1. Comp rend. 151, 359 (1910)
2. Comp rend. 151, 492 (1910)

EXPERIMENTAL.

Electric Furnace.

A piece of ordinary one inch iron pipe was cut to a length of forty inches. One end, at "A", was fitted with a pipe "T" and about eight inches of pipe fitted into this at right angles to the long pipe. The opposite end, at "B", was filed smooth and a condenser later fitted on. The pipe was covered with a layer of alundum cement about one-quarter of an inch in thickness, extending from the "T" to within an inch or two of the opposite end. The cement was allowed to dry thoroughly and then forty or fifty feet of #14 chromel "C" resistance wire was wound on this layer. Care was taken to have the coils of wire so placed as not to make contact; also, although the wire was wound tightly, it must not be wound tight enough to cut through the cement layer and thereby make contact with the metal. The coil was tied to the pipe firmly, leaving enough wire at both ends to make connections. Over this coil was plastered another layer of cement, of sufficient thickness to completely cover the wire. This layer was allowed to dry for about twenty-four hours and then thoroughly baked on by passing a current through the wire for an hour or so. After this treatment, there resulted a hard, firm cement layer and the pipe could be handled readily without danger of the cement falling off.

The bottoms were removed from five or six ordinary tin cans and these then fitted together so as to form a jacket, the length of which could be regulated. Holes were cut in

the center of two of the covers- just large enough to fit over the pipe and cement layer, these to serve as ends for the jacket. Two smaller holes were punched in one of the covers to hold small porcelain tubes, an inch or two long- made from broken porcelain triangles, to serve as insulators for the ends of the heating coil which are to be terminated outside of the jacket on suitable binding posts. This cover was fitted down over the pipe and cement layer to the pipe "T" at "A" and securely fastened there. Both ends of the nichrome wire were cleaned and spliced to separate pieces of #16 copper wire. The piece of copper wire at "A" need only be about sixteen inches long. The piece spliced to the resistance wire at "B" should be long enough to reach back to "A". This length is conducted back to "A" through a piece of capillary glass tubing, out through the porcelain insulator and fastened to a suitable binding post. The binding posts were bolted to a strip of wood which was wired to the upright piece of pipe. The shorter piece of copper wire was conducted out through the other insulator and fastened to the other binding post. The copper wire is more convenient to use on the outside of the jacket, since it does not heat up to any degree while the furnace is in operation. Care was taken to so bend those parts of the wires which were to be enclosed in the jacket, so that they would not make contact upon a slight jarring of the apparatus.

The jacket was slipped down over the pipe and fitted snugly to the cover at "A". This jacket was then filled with a quantity of "Sil-O-Cel" as a heat insulator and the cover

placed on at "B". The open end of the pipe "T" was fitted with a one by three-quarter inch bushing, carrying a well of sufficient length to extend about half way into the furnace, and sealed at that end. This smaller pipe was used to hold the pyrometer or thermometer. The jacket surrounding the furnace was covered with one thickness of ordinary steam-pipe covering and this fastened in place with metal bands.

When the furnace was wound for the first time, two coils of about #17 wire were used; arranged so that one was wound between the coils of the other. It was hoped that this arrangment might afford better temperature control, since one might pass current through one or both coils. In actual use, however, the furnace burned out twice with this arrangment - probably due to the fact that the coils were necessarily wound too close together, since about sixty feet of wire was used. About three feet of 12 mm. glass tubing was fastened to the pipe at "B" to serve as an air condenser.

Catalyst.

Sufficient pumice was ground to about pea size to fill the furnace to within an inch or two of the end. This was thoroughly soaked in water for 1-2 hours and then, while moist, rolled in 10-15 grs. of powdered aluminum oxide (c.p.) until the pieces were well coated with the catalyst. Ths furnace was then filled to within a few inches of the end, with this material. The smaller pieces were dropped in first so as to have that part surrounding the"well,"filled with the material.

In one or two runs, aluminum sulfate was used as a catalyst. The proceedure in this case was to boil the finely divided pumice with a saturated solution of aluminum sulfate for about one hour. It was then allowed to dry and used as in the case of the oxide.

The Effect of Aluminum Oxide on Phenol at High Temperatures.

In the first run the temperature of the furnace was 190-200 degrees. 100grs. of phenol was weighed into an ordinary distilling flask and distilled into the furnace thru the upright iron pipe. In this and the next two or three runs, a dark brown liquid distilled over - the color of which was probably due to the reduction of a quantity of rust in the pipe and the formation of oxidation products of phenol. Dense white fumes accompanied the liquid, which condensed only upon standing for an hour or so. The liquid distillate was shaken with strong NaOH solution. The entire distillate was soluble, and when again acidified and distilled, pure crystals of phenol were obtained, leaving a small amount of a black tarry substance

in the distilling flask. About 35 minutes were required in this run for the distillation of the phenol into the furnace.

A second run was made, again using 100 grs. of phenol and distilling it into the furnace at a temperature of 190-300 deg. The time required for distillation, however, was about 1½ hours. The distillate was again shaken with strong sodium hydroxide solution, acidified and the phenol recovered. The entire amount of distillate was soluble in the alkali and an amount of tar was again left upon recovery of the phenol.

Two other runs were made at this temperature, but with a lengthening of the time required to distill the phenol into the furnace. The longest time required was 2¼ hours. In each case practically all of the phenol was recovered, unchanged.

The furnace was then filled with a new supply of the catalyst. This time, however, the pumice was boiled for 1-2 hours with a thin paste of the aluminum oxide, then allowed to dry. This was done in hopes that the pores of the carrier might become impregnated with the catalyst, and the catalytic action thus be increased. The time required for this run was 2-2¼ hours.

Six subsequent runs were made at the following temperatures:- 200-210°; 240-260°; 280-300°; 330-350°; 365-375°; 400-425°. In no case, however, was any product other than phenol obtained.

Another method was tried- using 100 grs. of phenol and at a temperature of 460-490°. This consisted in inserting the end of the air condenser into a stopper and fitting this into a vacuum filter flask. Also, the pumice was packed into the furnace more tightly and a slight suction applied during the run.

In this way the rate of distillation of the phenol could be easily controlled. Three runs were made requiring about three hours each. In one case, upon the addition of the strong alkaline solution to the distillate, there separated out a small quantity of a brown precipitate. This was filtered off and a melting point taken. It melted at 80-83°; and burned leaving a black residue. A. Maihle describes the formation of diphenylene oxide by the action of thorium oxide on phenol at 475°, which compound melted at 82°. This therefore, was concluded to be diphenylene oxide- although there was only enough formed to take a melting point. The other two runs yielded only alkali soluble material and phenol was recovered from this in each case.

The action of aluminum sulfate on phenol at high temperatures.

Two runs were made using aluminum sulfate as a catalyst. 100 grs. of phenol was distilled into the furnace at 510-530° in three hours, a slight suction also being used. The products in both cases were alkali soluble and phenol was recovered.

Two runs were made using a dropping funnel. The phenol was dissolved in a small amount of benzene and dropped into the furnace slowly- instead of distilling it in. The temperature in this case was 450-460° and the time of the run was about 1½ hrs. This method of introducing the phenol was not very satisfactory, since the speed with which the mixture was introduced into the furnace could not be so readily controlled. The products were alkali soluble in both cases.

When working with temperatures below 350° a thermometer

was used. In all cases where the temperature was above 350°, a pyrometer was made use of.

SUMMARY.

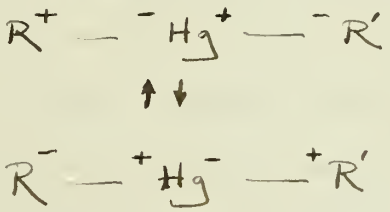
Several attempts have been made to prepare diphenyl ether catalytically, in an electric furnace, using aluminum oxide and aluminum sulfate as catalysts. Temperatures varying from 200°to 500° have been used. In no case was any diphenyl ether obtained. At 490°, aluminum oxide converts some phenol into diphenylene oxide. This seems to indicate that the catalytic formation of diphenyl ether is not possible- using aluminum oxide as a catalyst- since it decomposes into diphenylene oxide with a loss of hydrogen at any temperature high enough to cause the dehydration of the phenol.

Part II

Mixed Dialkyl Mercury Compounds.

INTRODUCTORY.

In a recent article, Jones and Werner described some work on aromatic mercury compounds,[1] from which they formulated a theory concerning the electronic structure of dialkyl and diaryl mercury compounds. Their assumption is that one of the valences functions positively and the other negatively. Thus, according to this, we may have compounds of the type:-



This work was undertaken in an attempt to prepare some mixed dialkyl mercury compounds, keeping in mind the possibility of the utilization of these as a proof of the types of valence on mercury in organic compounds.

1. J. Am. Chem. Soc. 40, 1257 (1918)

HISTORICAL.

Hilpert and Gruttner, in 1915, described the preparation of a number of dialkyl mercury compounds and, among them, benzyl ethyl mercury, which is the first mixed dialkyl mercury compound to be described.[1] This compound was prepared from:-

$$C_2H_5MgBr + \Phi CH_2HgCl \rightarrow \Phi CH_2HgC_2H_5 + MgBrCl$$

In the same paper, the following mixed alkyl-aryl compounds were described:- benzyl mercury phenyl, benzyl mercury ethyl, ethyl mercury phenyl and benzyl mercury o-tolyl.

A number of simple diaryl and dialkyl mercury compounds have been prepared. Duppa and Frankland describe the preparation of mercury diethyl and mercury dimethyl.[2] Wolff has prepared diphenyl mercury;[3] Pope and Gibson describe the preparation of dibenzyl mercury.[4] However with the exception of the work of Hilpert and Gruttner, very little is known concerning the mixed organic mercury compounds.

1. Ber. 48, 906 (1915)
2. Ann. 130, 105 (1865)
3. Ber. 48, 64 (1915)
4. J. Chem. Soc. 101, 735 (1912)

THEORETICAL.

If mercury in organic compounds really has one positive and one negative valence, a compound such as benzyl mercury methyl, upon treatment with hydrochloric acid, should hydrolyze in two different ways:-

(a) $C_6H_5CH_2^- - {}^+Hg^- - {}^+CH_3 + HCl \rightarrow C_6H_5CH_2HgCl + CH_4$

$\uparrow\downarrow$

(b) $C_6H_5CH_2^+ - {}^-Hg^+ - {}^-CH_3 + HCl \rightarrow C_6H_5CH_3 + CH_3HgCl$

In studying the reaction of the Grignard reagent on mercuric chloride, it has been found that one of the atoms of chlorine is much more easily replaced by an alkyl group than is the second atom.[1] It was thought that, by making use of this fact and preparing mixed dialkyl mercury compounds step-wise, the electronic isomers in this series might possibly be obtained. Thus, benzyl methyl mercury prepared in the following way might exist in two isomeric forms.

(1) $\phi CH_2MgCl + Cl\text{-}HgCl \rightarrow \phi CH_2HgCl + MgCl_2$

$\phi CH_2HgCl + CH_3MgI \rightarrow \phi CH_2HgCH_3 + MgICl$

(2) $CH_3MgI + Cl\text{-}Hg\text{-}Cl \rightarrow CH_3HgI + MgCl_2$

$CH_3HgI + \phi CH_2MgCl \rightarrow CH_3HgCH_2\phi + MgICl$

If the products obtained from these two series of reactions break down differently upon treatment with hydrochloric acid, or, if the products behave in the same way, but still give all of the decomposition products mentioned above (a,b), then the evidence furnished by these experiments would favor the theory of Jones and Werner.

1. Marvel and Gould- J. Am. Chem. Soc. January 1923.

However, if the products obtained from the above reactions behave in the same way toward acids and yield only one set of decomposition products, the evidence would not be so favorable to this theory.

After this work had been started, there appeared a paper by Kharasch and Jacobsohn,[1] in which the theory of Jones and Wærner was more or less conclusively disproved.

Due to the extremely harmful physiological action of these mercury compounds, it was found necessary to discontinue the work on this problem, before any conclusive results were obtained.

1. J. Am. Chem. Soc. 43, 1894 (1921)

EXPERIMENTAL.

Benzyl Mercury chloride.

a)Preparation of the Grignard reagent.

In a 500cc round bottom flask, fitted with a reflux condenser, is placed a mixture of 6 grs. of magnesium turnings and 200 cc of anhydrous ether. A separatory funnel is used to add, thru the condenser, 40 grs. of benzyl chloride- a crystal of iodine is also added, as a catalyst. Upon the addition of a few drops of the benzyl chloride and slight heating for a few minutes, the reaction begins and runs smoothly. The benzyl chloride is dropped in just fast enough to kepp the reaction going. The mixture is refluxed for about an hour, after the addition of the benzyl chloride. Any unchanged magnesium is removed by rapid filtration thru glass wool.

b) Reaction of the Grignard with mercuric chloride.

In a three-necked, three liter round bottom flask, fitted with a condenser and a mercury-seal stirrer, is placed a mixture of 80 grs. of dry,powdered mercuric chloride and 200 cc of dry ether. It was found advisable to add the mercuric chloride to the ether with continual stirring, so that it would not settle and form a cake at the bottom of the flask. The Grignard prepared above was added to this mixture, drop by drop, with continual stirring. The reaction mixture heats up during the addition of the Grignard, which may be added just rapid enough to keep the ether refluxing gently. After all the Grignard has been added, the mixture is refluxed on the steam-bath for 45 minutes. The flask is then cooled and 100-150 cc of water added, to decpmpose any excess Grignard reagent.

The mass is then filtered with suction, washed with water and a little dilute hydrochloric acid, sucked dry and recrystallized from boiling alcohol, separating in shiny leaflets-m.p. 104°
The mother liquors from the filtration were concentrated, the precipitate filtered off and treated as above. In all, 55 grs., 67% of the theory were obtained.

Notes:- Two runs were made in which the ether was distilled off from the final reaction mixture before any water was added. In both cases the yield was very small, seemingly due to a decomposition of the product during the distillation of the ether. It was found that prolonged refluxing after the addition of the Grignard reagent did not increase the yields; but the use of freshly prepared benzyl chloride, in making the Grignard was found to be advantageous.

Methyl Mercury Iodide

a) Preparation of the Grignard peagent.

In a 500 cc round bottom flask, fitted with a reflux condenser, is placed a mixture of 12 grs. of magnesium turnings and 200 cc of dry ether-a crystal of iodine is added as a catalyst. Thru the condenser, by means of a separatory funnel, 72 grs. of methyl iodide are gradually added. After the addition of a small amount of the methyl iodide and slight heating, the reaction runs smoothly and is finally completed by refluxing for about an hour. Any unchanged magnesium is filtered off rapidly through glass wool.

b) Reaction of the Grignard with mercuric chloride.

In a three-necked, three liter round bottom flask,

fitted with a reflux condenser and a mercury-seal stirrer, is placed a mixture of 140 grs. of mercuric chloride and 400 cc of anhydrous ether- observing the same precautions as in the preparation of benzyl chloride. The Grignard reagent was slowly added to this mixture, with continual stirring and after all of it had been added, the reaction mixture refluxed for about an hour. The flask was then cooled, and a small quantity of water added (25-30 cc). The ether was distilled off and the residue shaken with a mixture of 200 cc of water and 5 - 10 cc of hydrochloric acid. The mass was then filtered, washed and sucked dry on the Buchner funnel. The product contained an amount of mercuric iodide and two crystallizations from hot alcohol were necessary. The mother liquors yielded more product upon concentration. The crystals were slightly yellow in color and melted at 142-143°. The yield was 72% of the theory.

Notes:- the presence of a trace of mercuric iodide causes a slight red coloration; even upon recrystallization the product seems to decompose upon standing with the formation of an unknown red decomposition product.

Reaction of methyl magnesium iodide on benzyl mercury chloride.

a) Preparation of the Grignard Reagent.

This was prepared in the usual way from 2½ grs. of magnesium turnings; 15 grs. of methyl iodide and 150 cc of dry ether and the reaction mixture filtered rapidly thru glass wool.

b) Reaction of the Grignard with benzyl mercury chloride.

In a 500 cc round bottom flask fitten with a reflux condenser, was placed 100 cc of dry ether and 28 grs. of benzyl mercury chloride. To this mixture, the Grignard was slowly added.

The reaction mixture was refluxed for 12 hours. At the end of that time there was left a small amount of a white solid which was entirely insoluble in the ether. Upon addition of water to the solution there separated out a white crystalline substance, which melted over a range of four degrees- from 72°-76° Elementary analysis showed both iodine and chlorine to be present. It was probably a mixture of benzyl chloride and iodide and methyl chloride and iodide.

Notes:- Upon the addition of the Grignard reagent to the ether solution, a vigorous reaction took place which necessitated the cooling of the flask with ice.

Reaction of Ethyl Magnesium Bromide on Methyl Mercury Iodide

a) Preparation of the Grignard Reagent.

The reagent was prepared from 4 grs. of magnesium and 10.6 cc of ethyl bromide in 160 cc of dry ether, filtering the product thru glass wool to remove any unchanged magnesium.

b) Reaction of the Grignard with methyl mercury iodide.

In a 500 cc round bottom flask fitted with a reflux condenser, was placed a mixture of 42 grs. of methyl mercuric iodide and 150 cc of anhydrous ether. The Grignard was added slowly, through the condenser. There resulted a vigorous reaction which necessitated the cooling of the mixture, during the addition of the Grignard. It was then refluxed for three hours and allowed to stand over night. A small amount of insoluble material was left. 10-20 cc of water was added to the reaction product and the layers separated. The solid in the ethereal layer was filtered off and the filtrate distilled. A very small

quantity of solid was left in the distillation flask, and at no time did the temperature rise above 36°.
The solid was dried and an elementary analysis showed bromine and iodine to be present. It melted from 151°- 154° and was probably a mixture of ethyl mercuric bromide and methyl mercuric iodide.

No attempts were made to further identify the compounds resulting from these condensations- beacuse of the physiological action of them.

SUMMARY.

The Grignard reagent has been used in the preparation of alkyl mercury halides. However, the reaction between an alkyl mercury halide and the Grignard does not seem to run smoothly to give mixed mercury dialkyl compounds.

UNIVERSITY OF ILLINOIS-URBANA
3 0112 101353206